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Autoignition behavior of synthetic alternative jet fuels: An examination of chemical composition effects on ignition delays at low to intermediate temperatures

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Abstract

The autoignition characteristics of military aviation fuels (JP-5 and JP-8), proposed camelina-derived hydroprocessed renewable jet fuel replacements (HRJ-8 and HRJ-5), Fischer–Tropsch fuels (Shell and Sasol), three Sasol isoparaffinic solvents, as well as 50/50 volumetric blends of the alternative fuels with the conventional fuels are examined. Experiments were conducted in a rapid compression machine and shock tube at compressed temperatures of $625\text{ K} \leq T_c \leq 1000\text{ K}$, a compressed pressure of 20 bar, and under stoichiometric and lean conditions. Several implicit properties of the alternative fuels prompted a study of the influence of chemical composition on autoignition, including the influence of isoparaffinic, cycloparaffinic, and aromatic structures. In addition, interesting combustion phenomena at low-temperature conditions are investigated under lean conditions, specifically concerning jet fuel blend reactivity, where a convergence in blend reactivity to the reactivity of either a conventional or alternative fuel is observed. © 2014 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Keywords: Autoignition; Rapid compression machine; Shock tube; JP-8; JP-5

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1. Introduction

Commercial and military aviation are seeking to displace their current fuels with drop-in alter-

native fuels. Two attractive fuels are bio-derived hydroprocessed renewable jet (HRJ) and Fischer–Tropsch (FT). Because of the properties these fuels possess, they are targeted to be used as 50/50 blends with conventional jet fuel [1,2]. Certification of alternative fuels requires extensive testing and a thorough understanding of fuel physical and chemical properties. Understanding of the chemical kinetic behavior of alternative fuels, for example macroscopically exemplified through ignition delay, flame speed, and extinction limits, is needed for combustion model development. Kinetic targets for fuel characterization and model development have only become recently available in the literature for complex multi-component fuels, including autoignition studies for conventional, HRJ, and FT fuels [3–7]; however, little work has been performed regarding blends of conventional and alternative fuels. Additionally, the influence of fuel composition/structure on autoignition is sparse in the literature, particularly at lean conditions, that are becoming increasingly attractive for achieving reductions in production of harmful emissions. Here fuel structure–reactivity relationships are probed through the investigation of compositionally-unique solvents (§2.1).

The primary objective of this study is to examine the autoignition characteristics of alternative fuels (HRJ and FT) under low- and intermediate-temperature (<1000 K) conditions in a rapid compression machine (RCM) and shock tube. Secondly, the autoignition properties of compositionally-unique solvents are examined to characterize the impact of chemical structure on ignition delays. Finally, investigation of the autoignition of blends of conventional and alternative fuels is conducted at stoichiometric and lean conditions. Ignition delay measurements presented here are important for validation and improvement of future kinetic models, while examination of ignition delay chemistry for specific chemical structures will enhance understanding of structure–reactivity relationships; both of which contribute toward the successful integration of next-generation non-petroleum derived fuels into existing aviation systems.

2. Experimental methods

2.1. Test fuels and solvents

Two conventional military aviation fuels, JP-8 and JP-5, are the basis for comparison throughout this study, and were provided by the Air Force Research Laboratory at Wright Patterson Air Force Base and NAVAIR, respectively. In addition to JP-8 and JP-5, samples of camelina-derived HRJ fuels were provided and are designated as HRJ-8 and HRJ-5, where the

numeric digit corresponds to the conventional fuel designation. Also examined were five synthetic fuels: two FT fuels, Shell middle distillate synthesis kerosene (designated as “Shell”) and Sasol high temperature FT isoparaaffinic kerosene (designated as “Sasol”); and three solvents produced by Sasol, LPA-142, LPA-210, and LINPAR 1416-V. These five synthetic jet fuels were obtained from United Technologies Research Center, and represent a broad spectrum of specific chemical signatures of actual fuels. Additionally, in-house mixed 50/50 volumetric blends of each neat fuel, with JP-8 and JP-5 (HRJ-8 and HRJ-5 were blended only with their designated parent fuel) are also investigated. In total, 21 fuels were studied: two conventional, two hydroprocessed, five synthetic, and volumetric blends.

To examine the differences between the test fuels, normalized chromatograms for the neat fuels are shown in Fig. 1. The distinct peaks in the JP-8 chromatogram correspond to normal paraffins and are labeled for reference. The conventional jet fuels show a similar composition, with JP-5 a “narrower” cut compared to JP-8. HRJ-8 and HRJ-5 exhibit a similar composition in the lower carbon number range; however, HRJ-5 features an additional “hump” within the C_{15} – C_{17} range; this is not an anomaly of

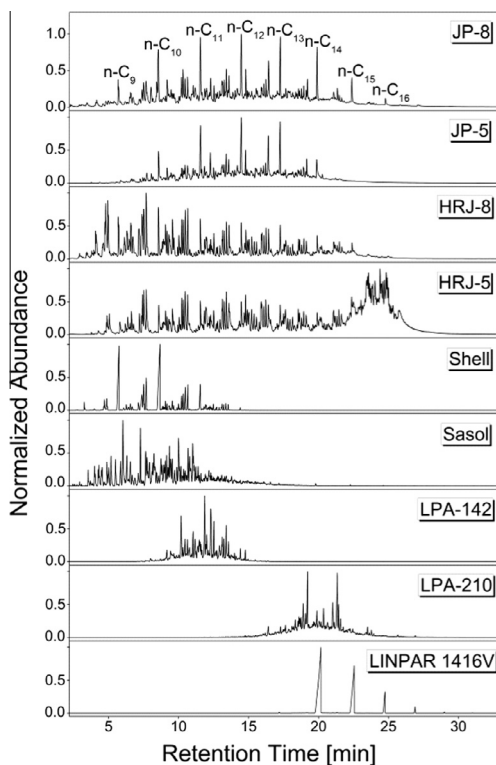


Fig. 1. Total ion chromatograms of fuels tested.

hydroprocessing, but an intentional addition of heavy paraffins to increase the flash point of the fuel to meet USN MILSPEC requirements. The FT fuels are narrower cuts in the lighter end of the boiling range of the conventional fuels. Shell contains prominent *n*-paraffinic content; however, Sasol does not show any apparent *n*-paraffin peaks. Examination of the solvent chromatograms indicates that LPA-210 and LINPAR 1416V are in the heavier end of the conventional jet fuel boiling range, while LPA-142 is lighter. Both the LPA fuels, categorized as isoparaffinic solvents, display no major *n*-paraffinic content. On the other hand, LINPAR1416V is completely composed of *n*-paraffins.

Table 1 displays selected physical and chemical properties of the test fuels and solvents. One major challenge with alternative fuels is meeting the military fuel density specifications. Table 1 shows that only the LPA solvents meet this specification, while the remaining fuels are below the lower density requirements of JP-8 and JP-5. Table 1 also displays that synthetic fuels either contain very little to no aromatics. Aromatics are important for providing the required swelling in elastomeric seals [8], requiring blending with conventional fuels to provide satisfactory aromatic content. These variations in properties inevitably lead to unique ignition behavior for each of the fuels as evident in the cetane index also given in Table 1. Generally, synthetic fuels have higher cetane index because of the overwhelming paraffinic content, however the influence of other chemical groups such as iso- or cycloparaffins, as well as olefins can greatly alter ignition properties. Differences among the test fuels and solvents physical and chemical properties motivate investigation into the autoignition characteristics of the fuels under different conditions.

2.2. Rapid compression machine: data analysis and experimental uncertainty

The main source of data collection for this study, specifically concerning low-temperature autoignition, involved the use of a RCM. Specifics on the RCM and methods used for low-volatile fuels are described in Allen et al. [9]. Briefly, fuel is loaded into the RCM using the direct test charge (DTC) method, where direct fuel injection occurs in the preheated combustion chamber four minutes prior to compression, to allow for a fully vaporized, zero-dimensional test platform. The ignition delay for RCM tests is defined from the start time, which is designated as top dead center (TDC), to the endpoint, which is when the peak pressure rise occurs. The pressure profiles recorded during testing employed a piezoelectric pressure transducer (Kistler 6125C) and are used to calculate the overall ignition delay (τ), where the start of combustion and peak pressure rise

event can be found using the first derivative of the pressure trace.

Compressed temperatures, T_c , are calculated at TDC and used as the reference temperature for comparing ignition delay experiments. A creviced piston, based on the design of Mittal and Sung [10] was used to eliminate significant boundary roll-up issues, thereby achieving an adiabatic core post-compression, allowing the calculation of compressed temperatures by, $\int_{T_0}^{T_c} \frac{\gamma}{\gamma-1} \frac{dT}{T} = \ln \frac{P_c}{P_0}$, where T is temperature, P is pressure, γ is the temperature-dependent specific heat ratio, and the subscripts 0 and c correspond to initial and compressed conditions, respectively. To solve for T_c , the temperature-dependent specific heat ratios for all gas-phase species must be known; however, the exact composition of the fuels tested is not practically quantifiable. In lieu of this data, the thermodynamic properties were approximated for JP-8 and JP-5 using surrogates proposed by Violi et al. [11] and Wood et al. [12], respectively. The former surrogate was verified in a kinetic model via comparisons to experimental data of premixed conventional kerosene flames, while the latter was experimental validated using a swirl-stabilized burner that showed similar combustion response between the surrogates and actual JP-5, except where soot formation was concerned. For the remaining fuels, T_c was calculated using the thermophysical properties of *n*-dodecane with a correction factor for each fuel, based on the fuel's estimated molecular weight ratio to *n*-dodecane. Thermophysical property data was found via Burcat [13] or by contribution methods [14], while molecular weights were estimated by the methods of Rao and Bardon [15]. Three ignition delay measurements tests have been performed at each condition and the standard deviations of the overall ignition delays at each measurement are represented by error bars when presenting results in this paper. The main uncertainty taken into account is from calculating compressed temperature, which accounted for only error in initial conditions and thermodynamic data and was determined to be $\pm 1.25\%$ (8–9 K).

2.3. Shock tube: data analysis and experimental uncertainty

A high-pressure shock tube at Rensselaer Polytechnic Institute was used to measure ignition delays at intermediate temperatures. Details of the shock tube and methods used for low-vol-

¹ Violi surrogate: 73.5% *n*-dodecane, 5.5% iso-octane, 10% methylcyclohexane, 10% toluene, 1% benzene.

² Wood surrogate: 2.5% *n*-decane, 25% *n*-dodecane, 10% *n*-tridecane, 5% *n*-tetradecane, 5% *n*-pentadecane, 11% *n*-pentylcyclohexane, 11% *n*-heptylcyclohexane, 11.5% decalin, 9.5% tetralin, 5% 1-phenylhexane, 3% 1,3-diisopropylbenzene, 1.5% α -methyl-naphthalene.

Table 1
Fuels/solvents physical and chemical properties.

Fuel	Cetane index	Flash Pt. (°C)	Density (g/mL)	Freezing Pt. (°C)	<i>n</i> -paraffins (%)	Isoparaffins (%)	Aromatics (%)
JP-8	~42–47	≥38	0.775–0.840	≤−47	32.6	30.2	15.7
JP-5	~39–48	≥60	0.788–0.845	≤−46	35.9	27.6	12.0
HRJ-8	58	43	0.752	−77	21.5	76.3	0
HRJ-5	66	62	0.768	−50	53.8	45.3	0
Shell	58	38	0.737	−54	41.0	59.0	0
Sasol	–	40	0.760	<−61	0.5	89.5	2.1
LPA-142	40.6	63	0.805	<−70	0	33.5	0
LPA-210	50.5	108	0.829	<−68	5.1	64.6	2.3
LINPAR 1416V	76.5	118	0.771	4	100	0	0

atility multi-component fuels are described by Wang and Oehlschlaeger [5] and references therein. In short, fuel is loaded into the shock tube using the conventional bulk preparation method, where fuel is pre-vaporized in a separate tank and fed into the shock tube prior to testing, allowing for a homogeneous test platform. Measurements of ignition time were made by monitoring pressure (side wall location 2 cm from end wall) and electronically-excited OH chemiluminescence around 306 nm (end wall location). The ignition time is defined as the time interval between shock arrival at the end wall, determined from the measured incident shock velocity and the time of passage at the side wall pressure transducer location, and the onset of ignition at the end wall, defined using the extrapolation of the maximum slope in end wall OH^{*} chemiluminescence to the baseline. All shock tube data is reported as individual data points with a reproducibility of 5–10% of the ignition delay.

Calculation of the incident and reflected shock conditions was performed using the normal shock relations and thermodynamic data for the compounds found in the jet fuel/air mixtures. Thermodynamic data for JP-8 was adopted from the Jet-A thermodynamic data found in the Goos et al. database [16]. For the remaining fuels thermophysical properties were formulated using group additivity, to match H/C, MW_{avg}, and distribution of organic structures found in these fuels as reported by Moses [17]. Following reflected-shock heating, the pressure was observed to rise at a rate of $(dP/dt)(1/P_0) = 1\text{--}3\% \text{ ms}^{-1}$ due to non-ideal gas dynamics. Uncertainty in the initial reflected shock temperature and pressure are estimated to be at most $\pm 1.5\%$ and $\pm 2\%$ (95% probability), respectively, based on the uncertainties in measured shock speed, initial conditions, and thermodynamic data. The uncertainty in ignition delay times is at most $\pm 25\%$, with the largest contributor to ignition delay uncertainty being temperature uncertainty.

3. Results and discussion

Ignition delays of the conventional (JP-5 and JP-8), HRJ (HRJ-5 and HRJ-8), FT (Shell and Sasol), solvents (LPA-142, LPA-210, and LINPAR 1416V) and 50/50 blends were studied at compressed temperatures of $625 \text{ K} \leq T_c \leq 1000 \text{ K}$, a compressed pressure of 20 bar, and equivalence ratios of $\phi = 1.0$ and 0.5. Additional measurements were conducted with the conventional and HRJ fuels at $\phi = 0.25$.

3.1. Comparison of conventional and alternative fuels in intermediate temperature range

Shock tube and RCM ignition delays for all fuels reported in this study, except HRJ-8, are presented in Fig. 2. All data in Fig. 2 are at $\phi = 1.0$; the shock tube data has been scaled to 20 bar using $\tau \sim 1/P_c$ to account for variations in compressed pressure (17–23 bar) and facilitate comparison. Open markers represent shock tube data, while filled markers RCM data. Overall, the shock tube and RCM data correlate favorably, with the exception of HRJ-5 and LINPAR 1416V where the RCM predicts faster ignition than the shock tube. This phenomenon has been previously noted [3,4], where ignition delays measured in RCMs can be shorter than observed in shock tubes for ignition delay times less than $\sim 8 \text{ ms}$ due to preignition chemistry occurring prior to TDC, particularly for highly reactive *n*-paraffinic fuels such as HRJ-5 and LINPAR 1416V.

As evident in Fig. 2, the fuels show different ignition characteristics as a function of temperature. At the lowest temperatures ($1000/T > 1.4$) conventional kinetic modeling for paraffins suggests that reactivity is controlled by low-temperature chain branching: $\text{R} + \text{O}_2 \leftrightarrow \text{RO}_2 \leftrightarrow \text{QOOH} + \text{O}_2 \leftrightarrow \text{OOQOOH} \rightarrow 2\text{OH} + \text{products}$. The rate of this reaction pathway is mostly governed by the $\text{R} + \text{O}_2 \leftrightarrow \text{RO}_2$ equilibrium and the rate of isomerization $\text{RO}_2 \leftrightarrow \text{QOOH}$. Figure 2 shows that the ignition delays of conventional fuels (JP-5 and JP-8) are very similar in the low tem-

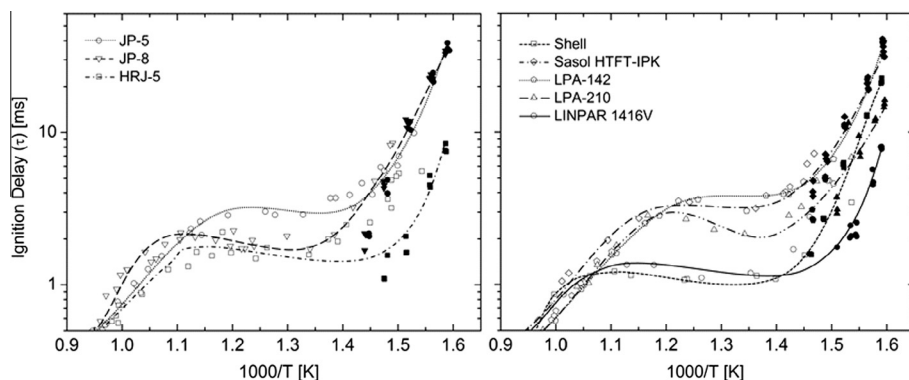


Fig. 2. Comparison of conventional and HRJ fuels (left) and FT and solvent fuels (right) at 20 bar, $\phi = 1.0$, and intermediate and low temperature conditions. Open markers represent the shock tube data. Filled markers represent RCM data.

perature region, due to their similar composition and hence low-temperature chemistry radical generation capabilities. The variation in ignition behavior observed for the other fuels and solvents is attributed to their different concentrations of *n*-paraffins, isoparaffins, and cycloparaffins, whose fractions control the global rate of low-temperature chain branching through the influence of different paraffinic bonding environments on the stability of RO_2 adducts and the rate of H-atom transfers in the $\text{RO}_2 \leftrightarrow \text{QOOH}$ isomerization. More detailed information on the effects of these chemical structures in the low-temperature chemistry region of the fuels studied will follow in §3.2–3.4.

Some of the trends observed in the low-temperature region are altered significantly in the intermediate-temperature negative-temperature-coefficient (NTC) region. The NTC region exhibits interesting behavior because a reduction in reaction rate is associated with an increase in temperature, which is believed to be the result of an equilibrium reaction that occurs between the formation and chain branching of hydroperoxides. As a result, intermediate-temperature chemistry increases in complexity because, in addition to the chain-branching low-temperature pathway outlined above, important radical propagation pathways play a role, including concerted HO_2 elimination from RO_2 and beta-scission of QOOH and cyclic ether formation from QOOH . The competition between low-temperature chain branching and these propagation pathways results in NTC behavior [18] and global fuel reactivity in this region is again dependent on the specific paraffinic bonding environment for these mostly paraffinic fuels. Aromatics in the fuel, which JP-5 and JP-8 both contain, generally scavenge radicals and slow ignition chemistry. One major difference in the NTC region is the drastic differences in the ignition delay times for the conventional fuels, where JP-8 appears to have a greater low-temperature activation energy, as evident in the higher

temperature requirement for onset of NTC (750 K) compared to JP-5 (730 K). One possible explanation for the discrepancy in their ignitions could be due to the amount of ortho-alkylaromatics present. Alkylaromatics with two ortho-alkyl groups or a long single lateral chain have the possibility of an internal transfer of a benzylic hydrogen and manifest a greater reactivity than aromatics that have neither ortho-alkyl groups nor a long lateral chain [19]. Another interesting observation in the NTC region is the LPA-210 solvent, which is fairly reactive at low-temperature conditions, shows low relative reactivity in its NTC temperature range (730–840 K), most likely attributed to the cycloparaffinic content. Aside from the conventional fuels and LPA-210, there are two generic groupings of fuels in the NTC region. The first is fuels with short ignition delays HRJ-8, LINPAR 1416V, and Shell, where their NTC to high-temperature transition temperatures are in the ranges of 700–880 K, 700–900 K, and 740–940 K, respectively; all three of these fuels contain a large amount of *n*-paraffins or lightly branched isoparaffins. The second is fuels with long ignition delay LPA-142 and Sasol, where their NTC to high-temperature transition temperatures are in the ranges of 725–830 K and 715–840 K, respectively; which contain mostly cycloparaffins or highly branched isoparaffins. At temperatures where the NTC behavior transitions to high-temperature behavior, the concentration of HO_2 increases which results in significant H_2O_2 formation via $\text{fuel} + \text{HO}_2 \leftrightarrow \text{H}_2\text{O}_2 + \text{R}$ and OH is liberated by $\text{H}_2\text{O}_2 + \text{M} \leftrightarrow 2\text{OH} + \text{M}$, ensuring rapid radical growth, short ignition delay, and a convergence in the autoignition behavior.

3.2. Comparison of conventional and alternative Fischer–Tropsch fuels

Figure 3 displays the low-temperature RCM data for the conventional, FT, and 50/50 volumetric

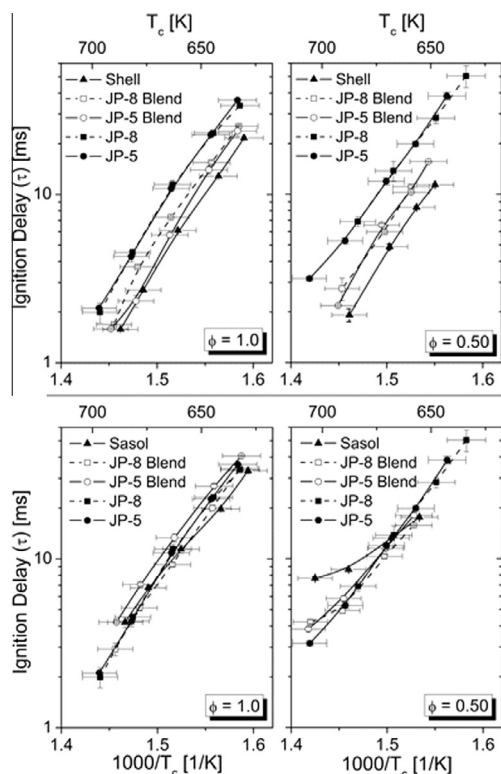


Fig. 3. Ignition delays for conventional and FT fuels at $P_c = 20$ bar and $\phi = 1.0$ (left) and 0.5 (right). The “JP-8 Blend” and “JP-5 Blend” represent the 50/50 volumetric blends on the neat FT fuel examined with a corresponding conventional fuel.

blends of the FT fuels with JP-8 and JP-5. Inspecting the neat Shell and conventional fuels ignition delays shows Shell has a shorter ignition delay at similar conditions, which correlates with the cetane index. Shell has a comparable chemical structure to the conventional fuels, but lacks aromatics and cycloparaffin content. Hence, the shorter ignition delay for Shell, composed of *n*- and isoparaffins with high reactivity associated with their potential for rapid radical production through the low-temperature chain branching mechanism due to large number of secondary C–H bonds providing relative RO_2 stability and rapid $RO_2 \leftrightarrow QOOH$ isomerization, compared to JP-8 and JP-5. The blends appear to be more similar in ignition delay to Shell, especially at lean conditions. This observation is likely the result of decreased inhibitive influence from aromatics at lean low-temperature conditions. In the presence of excess oxygen, aromatics can react directly with O_2 creating peroxy radicals and bridged structures, which fragment into smaller species thereby accelerating radical production and aromatic removal [20].

Examination of Sasol in Fig. 3 shows a dramatic difference in ignition relative to Shell, where Sasol has very similar ignition delay under

all conditions studied to the conventional fuels. Sasol almost completely consists of isoparaffins, which we hypothesize to be heavily branched in nature. Lightly branched paraffins react slower than their *n*-paraffin parent, but still generally have a relatively high reactivity due to the numerous secondarily bonded hydrogen atoms found in these compounds which aids in isomerization. However, for highly branched paraffins, the rate of isomerization is slower due to the fewer available secondary hydrogens for transfer through isomerization involving energetically preferred 6-membered transition states. As expected, the blend has very similar reactivity to the neat fuel at $\phi = 1.0$ as a result of Sasol’s comparability in ignition delay time to conventional fuels. However, under lean conditions, Sasol and the 50/50 blends appear to enter NTC region more rapidly than conventional fuels at $\phi = 0.5$. The intermediate temperature data in Fig. 2 displays that same trend occurring at $\phi = 1.0$ for Sasol at slightly higher temperatures.

3.3. Comparison of conventional fuels and solvents

Ignition delay measurements for the three solvents, LPA-142, LPA-210, and LINPAR 1416V, as well as the conventional fuels and corresponding 50/50 volumetric blends are presented in Fig. 4. Examination of LPA-142 shows similar ignition delays to JP-5 and JP-8 under all conditions studied. LPA-142 contains some isoparaffins, but has mostly cycloparaffinic content. At low temperatures, the oxidation of cyclo-components is significantly lower than that of an *n*-paraffin mainly due to the isomerization pathways and olefin formation. In comparison with non-cyclic structures, cyclic structures and resultant hydrogen distributions reduce the number of hydrogens available to the (1,5) H-shift, but retain abundant hydrogens for the (1,4) H-shift in the isomerization of fuel peroxy radicals, $RO_2 \rightarrow QOOH$, which results in the observed lower reactivity and higher olefin formation during low temperature oxidation [21]. As expected, the blend has very similar reactivity at all experimental conditions as a result of LPA-142’s similarity in delay time to conventional fuels.

Investigation of LPA-210 in Fig. 4 shows faster ignition at $\phi = 1.0$ relative to the conventional fuels. LPA-210 compositionally is almost completely isoparaffins and cycloparaffins with trace amounts of *n*-paraffins and aromatics. The experimental ignition delay occurring faster than the conventional fuels may be the result of two factors. The first is the higher carbon number range of LPA-210, where larger hydrocarbons generally ignite faster than smaller hydrocarbons under the same conditions, although this has been shown to have a limited effect [22]. Therefore, the majority of the increased reactivity of LPA-210 is attributed to

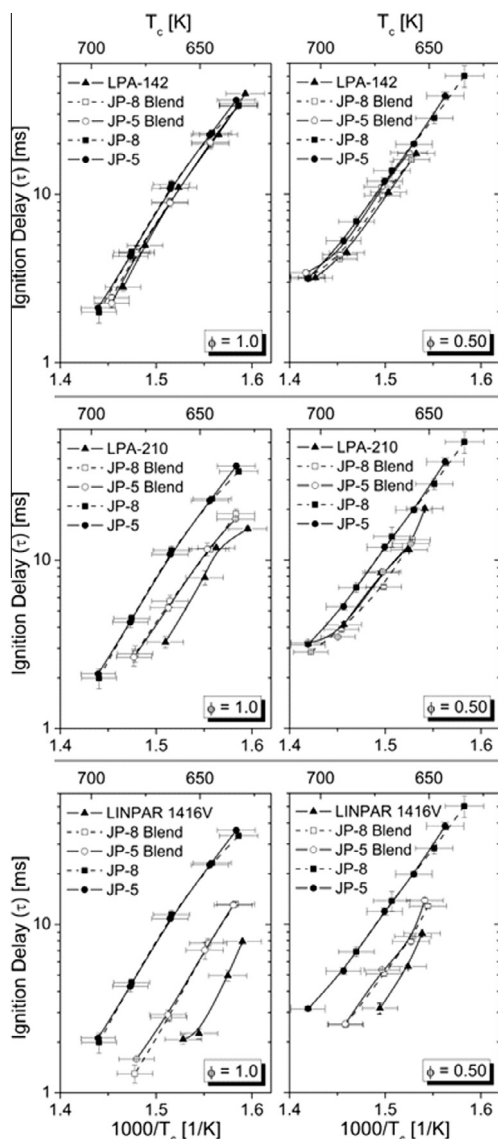


Fig. 4. Ignition delays for conventional and solvent fuels at $P_c = 20$ bar and $\phi = 1.0$ (left) and 0.5 (right). The “JP-8 Blend” and “JP-5 Blend” represent the 50/50 volumetric blends on the neat solvent examined with a corresponding conventional fuel.

the isoparaffins, which are hypothesized to be minimally to moderately branched. This hypothesis still allows the isoparaffins to contain substantial secondary hydrogens to aid in isomerization, allowing for faster ignition. The 50/50 blend has analogous reactivity to neat LPA-210, than the military fuels at $\phi = 1.0$ and $\phi = 0.5$. However, at $\phi = 0.5$, LPA-210 and the blend appear to approaching the reactivity of the conventional fuels. This could be the result of these fuels entering the NTC region earlier. Intermediate-temperature data showed that the LPA-210 has a very strong

NTC region, where a significant increase in delay occurs with temperature increase and these effects appear to be exacerbated at lean conditions.

The final solvent, LINPAR 1416V has significantly faster delays than the conventional fuels at all conditions studied, as evident in Fig. 4. This behavior was expected because of the high cetane index and long chained *n*-paraffins that LINPAR 1416 V contains, which should react rapidly in the low-temperature conditions because of ample secondary hydrogens. The blends appear to be more similar in ignition delay to the neat solvent at $\phi = 1.0$ and $\phi = 0.5$. Similar reasoning, as used in the explanation of this phenomena in §3.2, on the influence of lean conditions on aromatic reactivity, is hypothesized to cause the blends increased reactivity.

3.4. Comparison of conventional and proposed camelina-derived replacement fuels

Ignition delays for the conventional military aviation fuels, their proposed HRJ replacements, and the 50/50 volumetric blends of these fuels are depicted in Fig. 5. Examination of the USAF fuels shows that JP-8 ignites slower than HRJ-8 at all conditions as expected based on the cetane indices of the fuels, and the fact that HRJ-8 has a high paraffinic content, where the isoparaffins are lightly branched, and lacks aromatic content. A general trend that is observed is the influence of the equivalence ratio on the blend. Both neat fuels remain around the same difference of reactivity (~ 1.5 ms in ignition delay) as the equivalence ratio is reduced despite some deviation at the $\phi = 0.25$ condition, which exhibits a reduction in the overall activation energy in comparison to the $\phi = 1.0$ and $\phi = 0.5$ conditions. However, the blends do not maintain this reactivity difference, and appear to converge toward the reactivity of HRJ-8 at leaner conditions. A similar phenomenon is observed for the Shell and LINPAR 1416V fuels at lean conditions.

The USN neat fuels portray the expected behavior based upon their chemical compositions and cetane indices, with JP-5 having longer ignition delay than HRJ-5 at a given condition. However, the reverse behavior to that observed for the USAF fuels is detected for the USN fuels at reduced equivalence ratios. HRJ-5 converges toward the reactivity of JP-5 at leaner conditions, the opposite of the behavior seen in JP-8 and HRJ-8. A reduction in the overall activation energy at $\phi = 0.25$ is apparent in the USN fuels; however, this reduction in activation energy takes place at lower temperatures for HRJ-5 and the blend. One hypothesis for this behavior is that the HRJ-5 contains significant branching of higher carbon number isoparaffins, as indicated by the “hump” region in its chromatogram, which could lead to an earlier entrance into the NTC regime at lean low-temperature conditions.

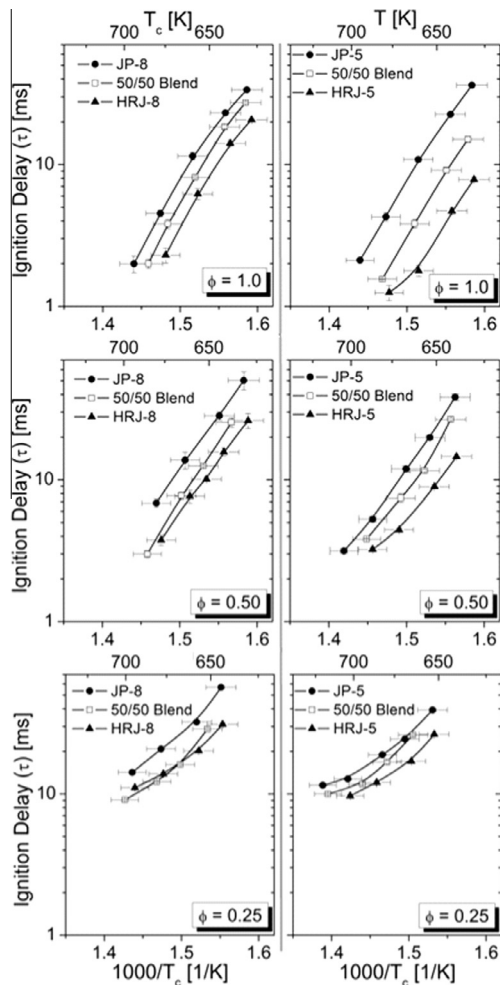


Fig. 5. Ignition delays for conventional military and HRJ fuels at $P_c = 20$ bar and $\phi = 1.0, 0.5$ and 0.25 .

4. Conclusions

In this study, the autoignition characteristics of two conventional military fuels (JP-5 and JP-8), two HRJ fuels (HRJ-5 and HRJ-8), two FT fuels (Shell and Sasol), three paraffinic solvents (LPA-142, LPA-210, and LINPAR 1416V) and 50/50 blends of the neat fuels with JP-5 and JP-8 have been investigated utilizing a RCM and shock tube at low to intermediate compressed temperatures, at a compressed pressure of 20 bar, and at fuel-lean and stoichiometric conditions. Examination of the chemical composition of each fuel and the corresponding effect on the ignition behavior was inferred. Specific behaviors that were prominent include the reduction in reactivity with increasing branching. In addition, the influence of cycloparaffin content on low- and intermediate-temperature ignition was observed, where cyclic-components result in more stable

intermediates, thereby decreasing reactivity. The influence of aromatic structure on ignition delay in different temperature regimes and effects of molecular oxygen to accelerate the fragmentation of aromatics at lean condition were also examined. Finally, the phenomenon of blend reactivity convergence toward a specific neat fuel, especially at lean conditions, was noted. The study motivates further investigation of chemical structure and multi-component fuel composition on ignition chemistry, especially under lean conditions and for blends of disparate fuels, to enhance combustion chemistry understanding and provide data for the improvement of kinetic models.

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